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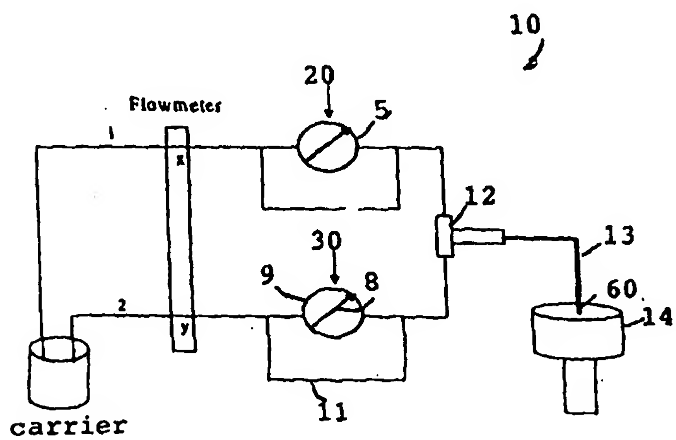
(54) Title: METHOD AND APPARATUS FOR PRODUCTION OF SMALL PARTICLES OF MICROMETER OR NANOMETER SIZE

(57) Abstract



The invention relates to a method for producing small particles of micrometer or nanometer size by means of mixing reagent solution (20) and a precipitating agent solution (30) together in a confined reaction zone (40), by using at least one carrier stream (50) segmenting the reaction zones (40), and subsequently contacting the solutions (20, 30) in the fluid carrier stream (50) together at a particular time interval T, reacting the metal ion solution (20) and the precipitating agent (30) under a limited period of time to form precipitates (60) of particles of small size, filtering the precipitates (60), and optionally drying and calcinating the precipitates (60) to form nanoparticle powder. The invention further relates to an apparatus, preferably a flow injection synthesis apparatus, for carrying out the method.

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Method and apparatus for production of small particles of micrometer or nanometer size

Field of the Invention

The present invention relates to a method for producing small particles of micrometer or nanometer size, and an apparatus for performing the method.

Background of the Invention

Reaction time and time of residence of the particles in a fluid reaction media, such as a bulk solution effects the shape and size of the particles. There are three periods in the generation of monodisperse particles for use as precipitation powders. The first is the induction time. The second is the nucleation period. The third is the growth period. After nucleation, during the third period, growth proceeds until the reaction stops due to the equilibrium. The size of nanoparticles in solution is very sensitive to the length of this period and the particles grow as the residence time increases. Depending upon the rate limiting step during growth, the particle size distribution may become narrower or remain constant as the particle growth proceeds.

The agglomeration or aggregation processes are especially important when the precipitation takes place in solution where particles have free contact to each other.

Thus, in order to obtain small particles which do not grow to larger particles, it is important to reduce the residence time in solution.

Summary of the Invention

The problem to be solved by means of the invention is to provide a method which permits reproducable conditions for the formation of small particles of micrometer and/or nanometer size and a drastically reduced residence time of the particles in solution while the production of particles proceed.

This problem is solved according to the invention by means of a method for producing small particles of micrometer and/or nanometer size in large quantities wherein the

precipitation is performed in confined reaction zones which are separated from each other.

According to a preferred embodiment of the invention, the method is performed by using a Flow Injection Synthesis (FIS) apparatus to be able to carry out the reaction in confined reaction zones, such as droplets, where agglomeration and aggregation can be limited.

By using FIS, the drawbacks are dramatically decreased or eliminated as the residence time is reduced to a few seconds, thus resulting in a smaller particle size and narrower particle size distribution.

According to a preferred embodiment of the invention, the method comprises the steps of:

- producing small particles of micrometer and/or nanometer size, by means of mixing at least one reagent solution, such as a metal ion solution and at least one precipitating agent solution together in one or more separated reaction zone(s), whereby the reaction zones are obtained by using a carrier fluid, for example water in the form of at least one stream, and providing the reaction zones, by injecting the solutions simultaneously in the carrier fluid at a particular time interval, at the same point in one carrier stream, or each solution in two synchronous carrier flowing streams, which are subsequently merged together, thereby segmenting the carrier stream(s),
- reacting the reagent solution and the precipitating agent solution under a limited period of time T to form precipitates of small particles, and optionally separating, e. g. filtering the precipitates, drying and calcinating the precipitates to obtain small particle powder, such as nanoparticle powder.

According to yet another preferred embodiment, the invention is embodied in an apparatus for production of small particles of micrometer and/or nanometer size, in particular nanoparticle powder, which apparatus comprises:

-pumping means for pumping at least one carrier fluid stream, preferably two, at a predetermined rate through at least one, preferably two tubes;
-injection means for introducing a reagent solution, such as a metal ion solution and a precipitating agent solution into the carrier fluid streams at a particular time interval T to obtain separated reaction zones, wherein
the apparatus is arranged to react the reagent solution and precipitating agent solution under a limited period of time to form precipitates, for instance by merging together the two fluid streams together, and optionally
separator means, such as filtering means is arranged to separate the precipitates from the carrier fluid stream.

The main advantage of FIS is that the particles so obtained can be extremely fine particles of about 10-20 nanometers (nm), where agglomerates are minimized or almost totally eliminated. Due to fact that the mixing pattern for a given set-up is perfectly reproducible, FIS yields reproducible results. FIS also can be used to study the behaviour of particulate solids in aqueous solution.

Preferably, the reaction is performed using a set of injection valves with controlled time and volume of solution to be injected into the reaction zones.

The solid particles may optionally be calcined to obtain small size particles.

The method has the advantage of controlled morphology and size, and is especially suitable for the production of nanoparticles.

Another advantage is that the synthesis is carried out via reactions in solution in confined zones, which are separated from each other by aqueous, non-aqueous, organic or gas phase. The particles as formed in the individual reaction zones are not brought in contact with other particles in other reaction zones.

Yet another advantage is that the solid particles are removed from the solution after a very short residence time from a few seconds to less than a few minutes.

Description of the drawings

In order to make the present invention easy to understand and produce, it will now be described with reference to the appended drawings, in which:

Fig. 1a shows a typical Flow Injection Analysis (FIA) peak from a recorder output.
Fig. 1b shows a schematic representation of confined reaction zone in a carrier fluid stream.
Fig. 2 shows a schematic block diagram of an embodiment of the apparatus according to the invention.
Fig. 3 shows synchronous merging of two zones in an FIS apparatus.

Detailed description of the Invention

Flow Injection Analysis (FIA) is widely applied in the area of the analytical chemistry. The conventional continuous flow analysis is based on the injection of a liquid sample into a moving, non-segmented continuous carrier stream of a suitable fluid, hereinafter called carrier stream. The analytical application of FIA includes detection through which a reaction is carried out in a confined segment between the required component and added reagents to form a product complex or species that can be detected - in a continuous matter by a suitable detector, e.g., colorimetric.

Fig. 1a shows a typical recorded output in the form of a peak, the height H of which is related to the concentration of the species indicating that the reaction has been confined to a limited volume of the carrier stream. The time period between the sample injection S and the peak maximum, which yields the analytical readout is the residence time T during which the chemical reaction takes place. The controlled dispersion of the sample zone which occurs during its passage through the system toward the detector results in a response curve the peak shape of which is characteristic of the FIA system. By changing the parameters, the dispersion can be manipulated easily to suit the requirements of a

particular chemical procedure so that optimum response is obtained at minimum time and reagent use.

Fig. 1b shows a schematic representation of confined reaction zone 40 in the carrier stream 50.

Flow injection synthesis (FIS) is based on the same principle and can be applied for carrying out reaction for the formation of solid particles. A flow injection manifold can be designed in which the different reactants are injected into a given reaction zone. The reaction conditions in each reaction zone can be easily adjusted to the chemistry required for the precipitation reaction. The reaction zones can be kept separated by a carrier stream. Subsequent additions of the reactants can be done after time T, again resulting in a separate reaction zone. In this case, particle growth takes only place through the interaction between particles within the same reaction zones and not from different reaction zones. By the proper selection of the reaction and mixing inside each reaction zone, particle growth can be significantly reduced. Moreover, a more uniform particle size can be obtained.

Fig. 2 shows a schematic block diagram of an embodiment of an apparatus 10 according to the invention. Reagent solution (metal ion solution) 20 and precipitating agent solution 30 (also called reactant solution below) were pumped from their individual containers (not shown) to the injection valves 5 of the apparatus 10 at a predetermined time interval T. This caused the resulting flowing carrier stream to be regularly segmented by water delivered from carrier 1 and 2, where the carrier streams are pumped at equal rates on lines 6 and 7 through tubes of equal length. By using multi-injection valves 5, solutions containing the different reactants are introduced into the rotating injection valves 5 comprising cavities 8 in a rotor 9, the length l and internal diameter d of which determine the reactant solution volume v. In the reactant injection position, the carrier stream is shunted through a by-pass line 11. After turning the rotor 9 to the injection position, an exact volume of reactant solution is swept by the carrier stream into the system, because the bypass has a higher hydrodynamic flow resistance than the solution line. The purpose

of using two injection valves 5 is to inject reactant solution into two separate carrier streams 1 and 2, for instance of water, pumped at the same speed, which then meet in a controlled way in a junction 12.

Alternatively, the two injection valves 5 can be combined in one multi injection valve, whereby only one carrier stream is required.

In Fig. 3 is shown a synchronous merging of the two solutions in the symmetrical system with continuous pumping: equal volumes of metal ion solution and precipitating agent solution are injected, and subsequently merged with identical velocities after passing through equal lengths of tubing, to continue downstream through line 13 while reaction takes place and precipitates are formed. Subsequently, the precipitates are passed through a solid-liquid separator 14 and the solid particles are collected.

The following steps of drying and calcination were similar to conventional bulk synthesis.

The main advantage of the flow injection technique is that the precipitation process is allowed to continue for a limited period of time T; a few seconds to a few minutes. The chemical reaction commences at the moment the solutions are mixed and the precipitation is completed in the confined zone. As shown in Fig. 2, two reactant solutions, are injected simultaneously into the carrier stream, and mixed together. The formed precipitate in the confined zone has the same composition as that obtained in bulk solution. The residence time is selected to allow the completion of the reaction. The precipitates are passed through the tube to a suitable solid/liquid separator, e.g. a filter. The particle in FIS technique has a residence time of only less than 2 min. In this way, the agglomeration is greatly limited, as the short residence time allows only the formation of the primary nucleation. The subsequent mixing of solutions, A and B, is done under identical conditions whereby powders with identical properties are obtained.

Claims

1. A method for production of small particles of micrometer and/or nanometer size, in particular nanoparticle powder, comprising the steps of:

- producing the small particles by means of mixing at least one reagent solution (20), such as a metal ion solution, and at least one precipitating agent solution (30) together in one or more separated reaction zone(s) (40), characterised in that the reaction zones (40) are obtained by using a carrier fluid (50), for example water in the form of at least one stream, and providing the reaction zones (40), by injecting the solutions (20, 30) simultaneously in the carrier fluid (50) at a particular time interval, at the same point in one carrier stream (50), or each solution (20, 30) in two synchronous carrier flowing streams (50), which are subsequently merged together, thereby segmenting the carrier stream(s) (50),
- reacting the reagent solution (20) and the precipitating agent solution (30) under a limited period of time T to form precipitates (60) of small particles, and optionally separating, e. g. filtering the precipitates (60), drying and calcinating the precipitates (60) to obtain small particle powder, such as nanoparticle powder.

2. A method according to claim 1, wherein the reaction time T is 1-2 minutes.

3. A method according to claim 1 or 2, wherein the method is performed by means of a flow injection synthesis apparatus (10), pumping at least one carrier stream (50) at a constant rate, wherein injection valves (5) are employed for injection of a predetermined amount of the reagent solution and the precipitating agent solution (20, 30) into the carrier fluid stream (50).

4. A method according to any one of the claims 1-3, wherein two or more synchronous carrier fluid streams (50) are employed.

5. An apparatus for production of small particles of micrometer and/or nanometer size, in particular nanoparticle powder, which apparatus comprises:

-pumping means for pumping at least one carrier fluid stream (50), preferably two, at a predetermined rate through at least one, preferably two tubes;
-injection means (5) for introducing a reagent solution, such as a metal ion solution (20) and a precipitating agent solution into (30) the carrier fluid streams (50) at a particular time interval T to obtain separated reaction zones (40), wherein
the apparatus is arranged to react the reagent solution and precipitating agent solution (20, 30) under a limited period of time to form precipitates (60), for instance by merging together the two fluid streams (50) together, and optionally
separator means, such as filtering means (14) is arranged to separate the precipitates (60) from the carrier fluid stream (50).

6. An apparatus according to claim 5, wherein the apparatus is a flow injection synthesis apparatus.

7. An apparatus according to claim 5 or 6, wherein the injection means (5) are rotary valves having cavities (8) intended to contain reagent solution and precipitating agent solution (20, 30).

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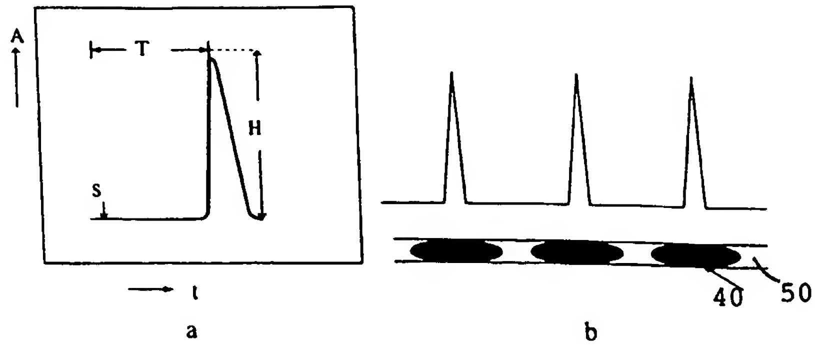
A
T
H
S
t
a
b
40
50

FIG 1

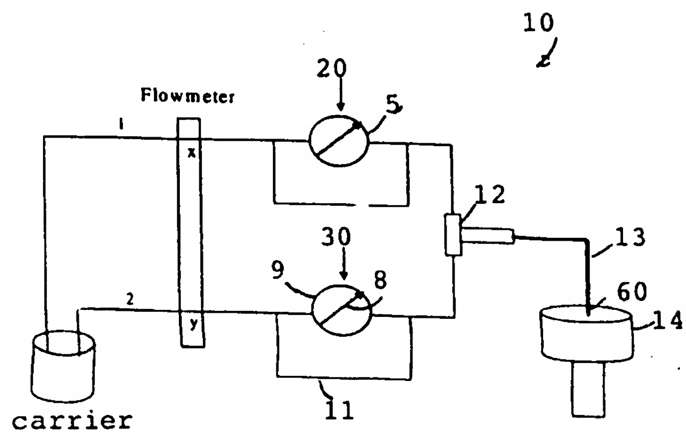
10
20
Flowmeter
5
1
x
12
30
13
9
8
2
60
y
14
carrier
11

FIG 2

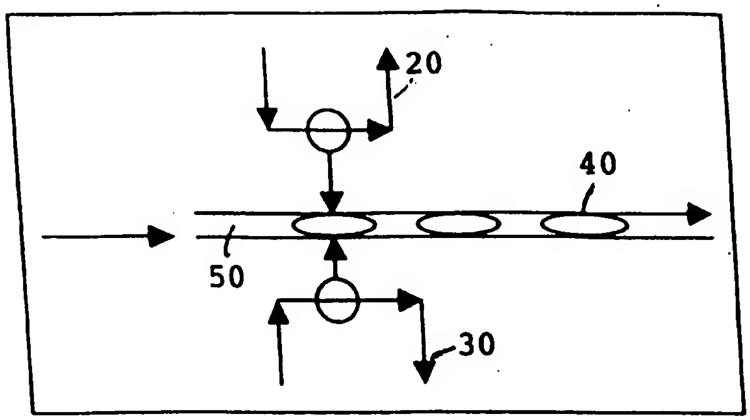

FIG 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE 99/01881

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: B01J 13/02, B22F 9/24
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: B01J, B22F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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PAJ, WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5652192 A (DEAN W. MATSON ET AL), 29 July 1997 (29.07.97), column 1, line 19 - line 22; column 3, line 22 - line 46, figures 1,2, claims 1-3 --	1-7
A	SE 502932 C2 (SANDVIK AB), 26 February 1996 (26.02.96), claim 1, abstract --	1-7
A	US 5166110 A (CLAUDE BRUN), 24 November 1992 (24.11.92), claim 1, abstract --	1-7
A	SE 502931 C2 (SANDVIK AB), 26 February 1996 (26.02.96), page 2, line 5 - line 35, claims 1,5, abstract --	1-7

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	TEKNIK I TIDEN, 1984: Vårvintern, Process i en vattendroppe, "Ny metod att tillverka mycket små metallpartiklar", page 15	1-7

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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